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URANIUM PURIFICATION BY THE PROCESS OF SALT TRANSPORT

by

J. B. Knighton, I. Johnson,
and R. K. Steunenberg

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Chemical Engineering Division

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ABSTRACT

An experimental investigation was conducted on the chemical aspects of a salt-transport process for the purification of uranium. Separations by means of salt transport are based on the selective transfer of a metallic solute from one liquid alloy to another by the circulation of a molten salt between the two alloys. Distribution-coefficient and solubility measurements were made to provide data needed to select suitable conditions for a uranium salt-transport process. Values are given for the distribution coefficients of uranium between molten MgCl_2 or MgCl_2 -alkali chloride mixtures and the following liquid alloys: Cu-Mg, Cu-Cd-Mg, Cd-Mg, Cd-Zn-Mg, and Zn-Mg. The solubilities of uranium in these liquid alloys are also reported. The advantages and disadvantages of various combinations of alloys and salts for a uranium purification process are discussed.

I. INTRODUCTION

The term "salt transport" has been applied to a purification technique whereby a metallic solute is transferred selectively from one liquid alloy (donor) to another liquid alloy (acceptor) by circulating a molten salt between the two alloys. The transfer takes place through oxidation of the solute by the salt at the donor alloy and its subsequent reduction by the acceptor alloy. The objective of the work described in this report was to investigate the chemical aspects of a uranium salt-transport step that could be incorporated into a pyrochemical process for fast breeder reactor fuels. Subsequent bench-scale engineering studies of the uranium salt-transport procedure that were based on the results of this study are covered in a separate report.¹ Although this work was directed primarily toward fuel reprocessing, the results may be useful for other applications, such as the preparation of high-purity uranium metal or the recovery of enriched uranium from scrap material.

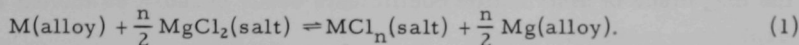
Various survey papers have been published on high-temperature liquid metal-molten salt extraction methods for the processing of nuclear reactor fuels.²⁻⁹ Certain investigations that were carried out earlier at Brookhaven National Laboratory and at Ames Laboratory are particularly relevant to salt-transport separations. The Brookhaven work involved a process that was being developed for the fuel of the proposed LMFR (Liquid Metal Fuel Reactor).¹⁰⁻¹³ This process employed a procedure in which UCl_3 in a molten salt phase was reduced selectively by a Bi-Mg alloy to separate uranium from rare earth fission products. The uranium was then reoxidized by a new salt stream and reduced again by Bi-Mg to form a Bi-Mg-U fuel alloy. At Ames Laboratory, Chiotti¹⁴ patented a salt-transport method for removing rare earth fission products from a Th-Mg alloy. The rare earths were selectively oxidized by MgCl_2 and subsequently removed from the MgCl_2 by reduction with a Zn-10 at. % (4 wt %) Mg alloy. This work was extended by Chiotti and Klepfer,¹⁵ who developed a salt-transport separation employing liquid Th-Mg and Zn-Mg alloys in mutual contact with a salt.

In the present studies, magnesium alloys of zinc, cadmium, and copper were investigated as potential donor and acceptor alloys for the purification of uranium by the salt-transport process. These studies included measurements of the solubility of uranium in the liquid alloys, and measurements of the distribution coefficient for uranium between molten salt mixtures containing MgCl_2 and liquid magnesium alloys. The effects of alloy composition and temperature on the solubility and distribution coefficient of uranium were determined. The dependence of the distribution coefficient on the salt composition was also studied.

II. CHEMICAL BASIS OF SALT-TRANSPORT SEPARATIONS

A. Partition of Solutes between Liquid Metals and Salts

The separation of uranium from impurity elements in a salt-transport process depends primarily upon differences in the distribution of uranium and the impurity elements between the liquid metal and salt solvents. In general terms, a metal, M, partitions between a liquid magnesium alloy and a molten salt phase containing MgCl_2 by the reaction



The thermodynamic (activity) equilibrium constant K_a can be expressed in terms of mole (or atom) fractions x and activity coefficients γ of the reactants and products as follows:

$$K_a = \frac{x_{\text{MCl}_n} x_{\text{Mg}}^{n/2} \gamma_{\text{MCl}_n} \gamma_{\text{Mg}}^{n/2}}{x_{\text{M}} x_{\text{MgCl}_2}^{n/2} \gamma_{\text{M}} \gamma_{\text{MgCl}_2}^{n/2}}. \quad (2)$$

The distribution coefficient D for the metal M is defined as the ratio of the mole fraction of MCl_n in the salt to the atom fraction of M in the alloy:

$$D = x_{\text{MCl}_n} / x_{\text{M}}. \quad (3)$$

The equilibrium constant K_a is related to the standard free energy change ΔG° for Reaction 1 by the equation

$$-RT \ln K_a = \Delta G^\circ = \Delta G_f^\circ \text{MCl}_n - \frac{n}{2} \Delta G_f^\circ \text{MgCl}_2, \quad (4)$$

where $\Delta G_f^\circ \text{MCl}_n$ and $\Delta G_f^\circ \text{MgCl}_2$ are the standard free energies of formation of MCl_n and MgCl_2 , respectively. Equation 4 indicates that metals whose chlorides have free energies of formation more negative than that of MgCl_2 (on a per mole of chlorine basis) will tend to distribute predominantly to the salt phase ($K_a > 1$). When the free energy of formation of MCl_n is less negative than that of MgCl_2 ($K_a < 1$), the metal M will tend to distribute to the alloy phase.

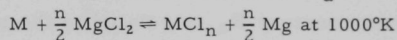
By substitution and rearrangement, the distribution coefficient may be expressed in logarithmic form as

$$\log D = \frac{\Delta G^\circ}{2.3RT} + \left(-\frac{n}{2} \log a_{\text{Mg}} + \log \gamma_{\text{M}} \right) - \left(-\frac{n}{2} \log a_{\text{MgCl}_2} + \log \gamma_{\text{MCl}_n} \right), \quad (5)$$

where three groups of terms are shown on the right-hand side. The first group, the single term $\Delta G^\circ/2.3RT$, depends both on the value of the free energy of formation of MCl_n relative to the value for $MgCl_2$ and on the temperature. The second group of terms, $-\frac{n}{2} \log a_{Mg} + \log \gamma_M$, depends on the composition of the liquid magnesium alloy and on the temperature; it is independent of the salt composition. The last group depends on the composition of the salt and on the temperature. In general, the distribution coefficients of various elements fall in the same order as the free energies of formation of their chlorides. However, significant changes in the magnitude of distribution coefficients occur because of solvent effects.

In the case of uranium, most of the thermodynamic quantities in Eq. 5 are available from other sources, such as high-temperature measurements in galvanic cells and solubility studies. Estimates¹⁶ of the distribution of uranium from these data are in very good agreement with direct experimental determinations. Only a limited amount of data is available on activity coefficients of other metals in liquid alloys and their chlorides in molten salt mixtures. Therefore, their distribution behavior can be predicted only approximately from their free energies of formation. Examination of a tabulation (see Table I) of free energies of formation of fission product metals and structural materials reveals that the salt-transport process should be particularly useful for the separation of uranium from the noble and refractory fission product metals (Zr, Nb, Mo, Tc, Ru, Rh, and Pd), and from metals such as iron, chromium, and nickel, which are typical constituents of alloys used to clad nuclear reactor fuel elements.

TABLE I. Standard Free Energies of Formation of Chlorides and Thermodynamic Equilibrium Constants K_a for the Reaction



MCl_n	$-\Delta G_f^\circ$ (kcal/g-equiv Cl)	K_a	MCl_n	$-\Delta G_f^\circ$ (kcal/g-equiv Cl)	K_a
BaCl ₂	83.4	$1.7 \cdot 10^{11}$	MgCl ₂	57.7	1.00
KCl	81.4	$1.5 \cdot 10^5$	UCl ₃	54.0	$3.8 \cdot 10^{-3}$
RbCl	81.2	$1.4 \cdot 10^5$	ZrCl ₂	49.2	$1.9 \cdot 10^{-4}$
SrCl ₂	81.0	$1.5 \cdot 10^{10}$	MnCl ₂	42.3	$1.9 \cdot 10^{-7}$
CsCl	80.0	$7.5 \cdot 10^4$	ZnCl ₂	35.0	$1.2 \cdot 10^{-10}$
SmCl ₂	80.0	$5.6 \cdot 10^9$	CrCl ₂	31.9	$5.3 \cdot 10^{-12}$
LiCl	78.8	$4.1 \cdot 10^4$	CdCl ₂	30.4	$1.2 \cdot 10^{-12}$
CaCl ₂	77.9	$6.8 \cdot 10^8$	FeCl ₂	26.6	$2.5 \cdot 10^{-14}$
NaCl	75.7	$8.6 \cdot 10^3$	NbCl ₅	24.6	$6.8 \cdot 10^{-37}$
LaCl ₃	67.0	$1.3 \cdot 10^6$	CuCl	22.0	$1.6 \cdot 10^{-8}$
PrCl ₃	66.3	$4.4 \cdot 10^5$	NiCl ₂	20.0	$3.3 \cdot 10^{-17}$
CeCl ₃	66.3	$4.4 \cdot 10^5$	MoCl ₂	8.0	$1.9 \cdot 10^{-22}$
ThCl ₃	65.3	$9.6 \cdot 10^4$	TcCl ₃	7.0	$5.7 \cdot 10^{-34}$
NdCl ₃	64.2	$1.8 \cdot 10^4$	RhCl	5.8	$4.5 \cdot 10^{-12}$
YCl ₃	61.2	$2.0 \cdot 10^2$	PdCl ₂	3.8	$2.8 \cdot 10^{-24}$
PuCl ₃	58.9	6.1	RuCl ₃	1.4	$1.2 \cdot 10^{-37}$

The difference in the distribution behavior of two elements, M_a and M_b , is expressed quantitatively as a separation factor

$$\alpha = D_{M_a}/D_{M_b}. \quad (6)$$

The separation factor is strongly dependent on the composition of the liquid alloy, and to a lesser extent on the temperature and on the composition of the molten salt.

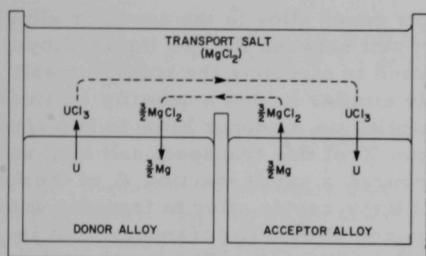
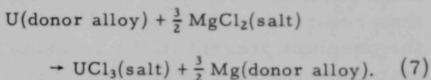


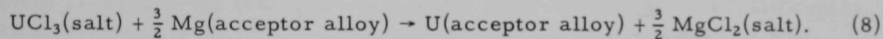
Fig. 1. Schematic Illustration of a Salt-transport Process for Uranium

B. Salt-transport Separations

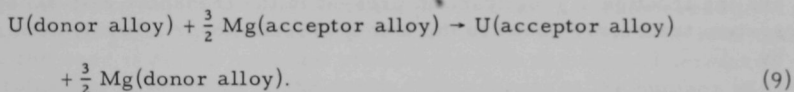
A salt-transport procedure for uranium is illustrated schematically in Fig. 1. Metallic uranium, which is initially present in the donor alloy, is oxidized and extracted into the transport salt:



When the transport salt containing the UCl_3 is contacted with the acceptor alloy, the reverse reaction takes place:



Therefore, the net reaction is



For each mole of uranium transferred from the donor alloy to the acceptor alloy, 1.5 moles of magnesium are transferred in the opposite direction. The increasing concentration of magnesium in the donor alloy and magnesium depletion in the acceptor alloy must be taken into account in the design of a practical process.

When Reaction 9 has reached equilibrium, both alloys are in equilibrium with the transport-salt phase, and the ratio R of uranium in solution in the acceptor and donor alloys is equal to the ratio of the distribution coefficients of uranium for each alloy and the salt:

$$R = \frac{\text{at. \% U in acceptor alloy}}{\text{at. \% U in donor alloy}} = \frac{D(\text{donor alloy})}{D(\text{acceptor alloy})}. \quad (10)$$

In principle, it might be possible to select salt-alloy systems in which the value of R is high for uranium and low for the impurities, in which case the impurities would remain in the donor alloy when the system reaches equilibrium. However, this is rarely, if ever, possible in a practical separation process, since a system that gives a large value of R for uranium is likely to have a similarly large value for the impurities. Instead, the separation is achieved through differences in the rates at which uranium and the impurities are transported.

The transfer of uranium from the donor alloy to the acceptor alloy is achieved by circulating the transport salt between the two liquid alloys. Although a variety of methods may be used to circulate the transport salt between the two alloys, all are basically similar in that a quantity n_S (moles) of transport salt is contacted with a quantity n_D of donor alloy to transfer uranium to the transport salt. A fraction X of this transport salt and, under some conditions (i.e., if entrainment occurs), a small fraction Z of the donor alloy is contacted with a quantity n_A of the acceptor alloy to transfer uranium from the transport salt to the acceptor alloy. The transport salt is then returned to the donor alloy to complete the cycle. The fraction F_D of the uranium present in the transport salt-donor system that transfers to the transport salt-acceptor alloy system is given by

$$F_D = \frac{D_D \frac{n_S}{n_D} X + Z}{D_D \frac{n_S}{n_D} + 1}, \quad (11)$$

and the fraction F_A of uranium present in the transport salt-acceptor alloy system transferred back to the transport salt-donor alloy system is given by

$$F_A = \frac{D_A \frac{n_S}{n_A} X + Z}{D_A \frac{n_S}{n_A} + 1}, \quad (12)$$

where D_D and D_A are the distribution coefficients of uranium for the transport salt-donor alloy and transport salt-acceptor alloy systems, respectively. It may be shown that after s cycles, corresponding to the circulation of a quantity $n_S X$ of transport salt, that the fraction Φ of the uranium initially present in the transport salt-donor system transferred to the transport salt-acceptor alloy system is given by

$$\Phi = \left(1 - \frac{F_A}{1 - F}\right)(1 - F^S), \quad (13)$$

where $F = (1 - F_D)(1 - F_A)$ (if it is assumed that no uranium is present initially in the acceptor alloy). Equation 13 indicates that the fraction of uranium transferred approaches a limiting value (given by the first factor) as the number of cycles, or the quantity of salt cycled, is increased. The maximum possible fraction Φ_{\max} transferred is given by

$$\Phi_{\max} = 1 - \frac{F_A}{1 - F} \approx 1 - \frac{D_A n_D}{D_D n_A}, \quad (14)$$

where the approximation is good to about 1%.

Equation 14 indicates that if the ratio n_A/n_D is unity, then, for a 99% transfer, D_D should be about 100 times D_A . The number of cycles, or the quantity of transport salt cycled to achieve a given percentage of the maximum possible transfer, is dependent only on the value of F . For example, to reach 99% of the maximum possible transfer when $F = 0.5$ requires about seven cycles, whereas when $F = 0.7$, 13 cycles are required. Large values of D_D favor rapid transfer of uranium.

Equations 11 to 14 are derived on the assumption that all the uranium present in the transport salt-donor alloy or transport salt-acceptor alloy systems is in solution, either in the alloys or the transport salt. However, uranium has a limited solubility in several usable alloys. If the uranium present in the transport salt-donor alloy system is not all in solution, then the fraction of the total uranium present that is transferred to the acceptor alloy during each cycle of the transport salt would be less than would be the case if all the uranium present were in solution. Therefore, limited solubility of uranium in the donor alloy increases the number of cycles of transport salt required to transfer a given fraction of the uranium to the acceptor alloy. The quantity of uranium transferred from the donor alloy to the acceptor alloy during each cycle will be constant (assuming equilibrium is established) until sufficient uranium has been transferred so that the amount remaining is completely in solution.

If the uranium has a limited solubility in the acceptor alloy, the acceptor alloy will become saturated after a few cycles of the transport salt and the amount of uranium back-transferred to the donor alloy will reach a constant value. This constant value is lower with a saturated acceptor alloy than it would be if the amount of uranium in solution in the acceptor increased with each cycle of the transport salt. The overall effect of limited solubility in the acceptor alloy is to decrease the number of transport-salt cycles needed to transfer a given fraction of uranium. The maximum possible fraction transferred may also be increased by limiting the uranium solubility in the acceptor alloy. Thus, in Eq. 14, the term $D_A n_D / D_D n_A$ is

multiplied by the solubility of uranium in the acceptor alloy expressed as a fraction of the uranium initially charged to the system. A low solubility of uranium in the acceptor alloy can be used to compensate for a large value of the distribution coefficient D_A .

The fraction of the uranium initially present in the transport salt-donor alloy system that may be transferred to the acceptor alloy may be increased if the uranium present initially exceeds the solubility. For example, in a system in which a maximum transfer of 97% is possible when the donor alloy is initially just saturated with uranium, the amount transferred may be increased to 99% by increasing the amount of uranium present to five times the solubility limit. However, the number of transport-salt cycles required is increased from about 13 for the case of 97% transfer to about 21 for 99% transfer.

The same principles that govern the rate of transfer of uranium apply to the impurities that are present in the donor alloy. Impurities for which the value of F_D (see Eq. 11) is small compared with the value of F_D for uranium are separated from uranium by the salt-transport process. Generally these impurities are those for which the value of D_D is smaller by several orders of magnitude than the value of D_D for uranium. An estimate of the decontamination factor, D.F., possible with the salt-transport process can be obtained from the expression

$$D.F. = \frac{\Phi(\text{uranium})}{\Phi(\text{impurity})}. \quad (15)$$

The fraction of uranium transferred, $\Phi(\text{uranium})$, will be approximately unity, i.e., essentially all of the uranium will be transferred. For small values of F_D , the quantity $\Phi(\text{impurity})$ (see Eq. 13) is approximately equal to sF_D' , where s is the number of cycles needed to transfer the desired fraction of uranium and F_D' is the fraction of impurity transferred from the donor. Substitution in Eq. 15 gives

$$D.F. \approx \frac{1}{s \left(D_D' \frac{n_S}{n_D} X + Z \right)}, \quad (16)$$

which summarizes most of the important factors that influence the degree of decontamination obtainable with the salt-transport process. The D.F. is inversely proportional to the number of transport-salt cycles, s , or the amount of salt circulated, to achieve the desired uranium transfer. It is also seen that the fraction of donor alloy entrained with the transport salt must be smaller than $D_D'(n_S/n_D)X$ if the maximum possible decontamination is to be achieved. The small values of D_D' for the noble and refractory metal fission products (see K_a values in Table I) indicate that the D.F. in practical systems will depend upon the extent to which entrainment of the donor alloy with the transport salt can be eliminated.

III. DONOR ALLOYS

A. Copper-Magnesium

The copper-magnesium system has a number of characteristics that make it suitable as a donor alloy for a uranium salt-transport separation. It was indicated earlier that the amount of uranium that can be transferred in each cycle of the transport salt between the donor and acceptor alloys depends upon the amount of salt transferred and the uranium content of the salt. At equilibrium, the uranium content of the transport salt is the product of the uranium content of the alloy and the distribution coefficient:

$$\text{at. \% U(salt)} = \text{at. \% U(metal)} \times D_D. \quad (17)$$

In a practical process, the donor alloy would ordinarily be saturated with uranium through most of the operation. The solubility of uranium in the donor alloy and the uranium distribution coefficient should have large values to achieve a large uranium content in the transport salt.

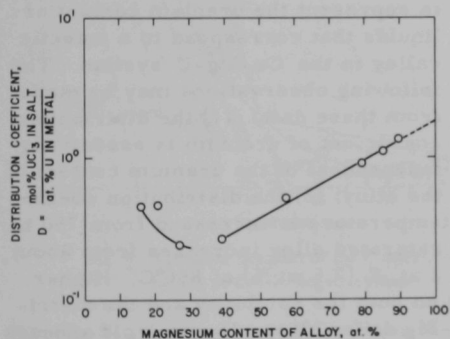


Fig. 2. Distribution of Uranium between MgCl_2 Salt and Cu-Mg Alloy at 800°C

The solubility of uranium in a Cu-Mg alloy and the uranium distribution coefficient are both affected by the magnesium content of the alloy and the temperature. Figure 2* shows the distribution of uranium at 800°C between liquid MgCl_2 and uranium-saturated Cu-Mg alloys of varying magnesium content. As the magnesium content of the alloy increases, the uranium distribution coefficient decreases at first, and then increases gradually at the higher magnesium concentrations.

The effect of magnesium content on the solubility of uranium in the Cu-Mg alloy at 800°C is indicated in Fig. 3. The data in Fig. 3 represent the composition of the liquid in equilibrium with a solid that contains uranium for the 800°C isotherm in the Cu-Mg-U system. The composition of the solid in equilibrium with the liquid was not determined. The missing portions of the curves in Figs. 2 and 3 [below 15.8 at. % (6.5 wt %) magnesium and from 30.1 at. % Mg (14 wt % Mg) to 38.2 at. % Mg (19 wt % Mg)] correspond to composition ranges within which liquids do not exist in the Cu-Mg-U system at 800°C .

*Detailed data upon which this and other subsequent figures are based are given in the Appendix.

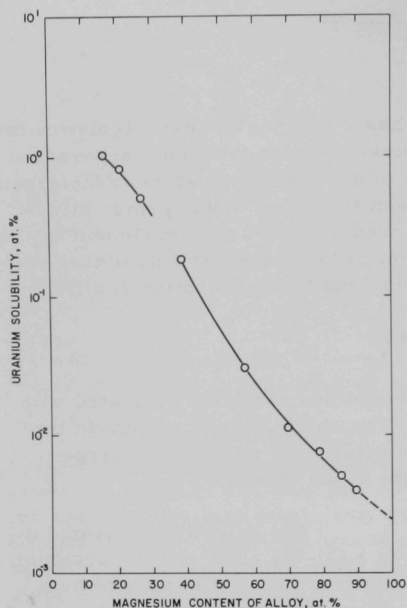


Fig. 3. Solubility of Uranium in Cu-Mg Alloy at 800°C

coefficient increases about twofold as the temperature is increased from 750 to 850°C; (3) the uranium content of the saturated alloy increases from about 0.5 at. % (2.1 wt %) at 750°C to about 2 at. % (7.6 wt %) at 850°C. Higher temperatures have a desirable effect on both the solubility and the distribution coefficient of uranium in a Cu-Mg donor alloy. However, it appears that other considerations such as the volatility of magnesium and the availability of suitable containment materials will limit the maximum practical operating temperature for a Cu-Mg donor alloy to about 900°C.

The distribution coefficient and solubility of uranium are most favorable for uranium transport at low magnesium concentrations. Although the distribution coefficient becomes sufficiently large again at high magnesium concentrations, the solubility of uranium is too low at these concentrations for a practical process.

Figure 4 shows the effects of temperature and of uranium content of a copper-rich Cu-Mg-U alloy on the distribution coefficient of uranium for a MgCl_2 salt phase and the alloy. The distribution coefficients at 750, 800, and 850°C are plotted as a function of the uranium content of the liquid metal phase. The curve A'A is believed to represent the uranium content of liquids that correspond to a eutectic valley in the Cu-Mg-U system. The following observations may be made from these data: (1) the distribution coefficient of uranium is essentially independent of the uranium content of the alloy; (2) the distribution coefficient

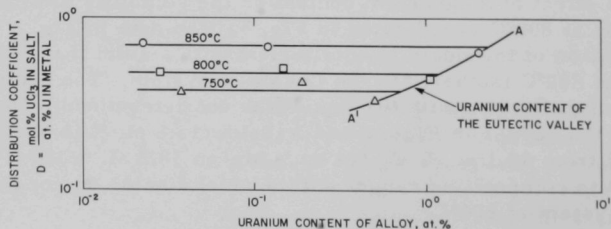


Fig. 4. Distribution of Uranium between MgCl_2 Salt and Cu-Mg Alloys at 750, 800, and 850°C

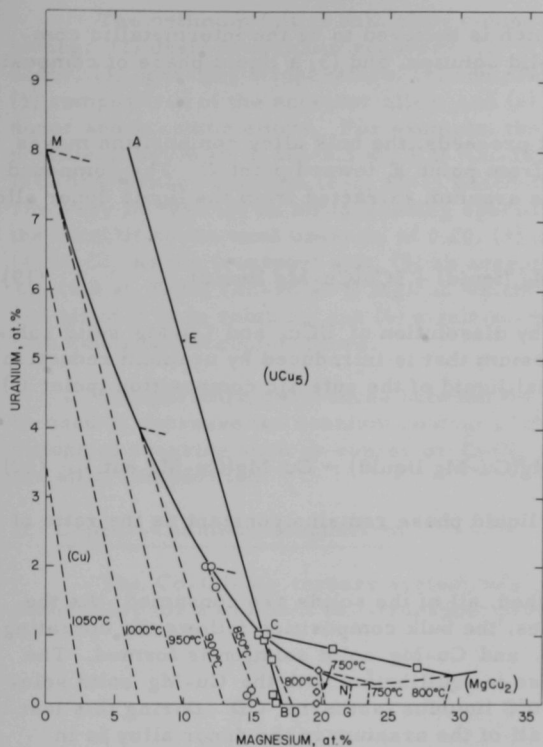


Fig. 5. Tentative Diagram of the Copper-rich Region of the Cu-Mg-U System

the Cu-Mg binary at 800°C. Point C is the 800°C liquidus on the eutectic valley, and CD is the 800°C liquidus isotherm between the eutectic valley and the Cu-Mg binary. Line AB is an operating line that is the path that the bulk composition of the donor alloy will follow as the transport of uranium takes place. The line represents the change in bulk composition that results from depletion of the uranium by MgCl_2 oxidation and the resultant buildup of magnesium in the donor alloy. These composition changes are related by the equation

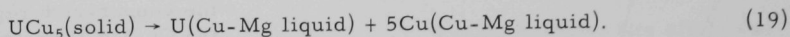


which indicates that 1.5 moles of magnesium are introduced into the donor alloy for each mole of uranium removed. Any point, such as E, lying on the operating line represents an initial bulk composition of the donor alloy. Point B is the bulk composition of the donor alloy upon completion of uranium transport. At point E the equilibrium phases present are (1) a solid

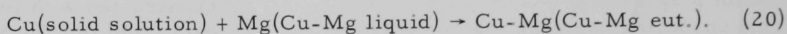
It was indicated earlier that a Cu-Mg donor alloy for a uranium salt transport process must have a low magnesium content. The operation of the Cu-Mg-U system as a uranium donor alloy is best illustrated by referring to the copper-rich region of the Cu-Mg-U system as shown in Fig. 5. This representation of the copper-rich region of the ternary system must be regarded as tentative because it was constructed with limited data from the Cu-Mg-U ternary and the Cu-U and Cu-Mg binary systems. The system is described below. Point M is an eutectic in the Cu-U binary alloy. Point G is an eutectic in the Cu-Mg binary alloy. Point N is estimated to be the ternary Cu-Mg-U eutectic. Hence, the curve MCN describes an eutectic valley. Point D is the composition of the liquidus of

phase containing uranium, which is believed to be the intermetallic compound UCu_5 , (2) a Cu-Mg solid solution, and (3) a liquid phase of composition C.

As uranium transport proceeds, the bulk alloy composition moves along the operating line AB from point E toward point C. The compound UCu_5 dissolves, replacing the uranium extracted from the liquid donor alloy by the transport salt:



The copper released by dissolution of UCu_5 and Cu-Mg solid solution combines with the magnesium that is introduced by uranium reduction of MgCl_2 to produce additional liquid of the eutectic composition (point C) at the operating temperature:



Thus, the composition of the liquid phase remains constant as the ratio of liquid to solids increases.

When point C is reached, all of the solids are consumed. As the transport of uranium continues, the bulk composition follows the operating line from point C to point B, and Cu-Mg solid solution is formed. The composition of the liquid phase in equilibrium with the Cu-Mg solid solution is represented by the 800°C liquidus isotherm, CD. During this last phase of uranium transport, all of the uranium in the donor alloy is in solution.

To control the magnesium buildup in the donor alloy during uranium transport, the operating line should pass through the liquidus on the eutectic valley at the operating temperature. This liquidus composition on the eutectic valley is the composition the liquid phase will have as UCu_5 and Mg-Cu solid solution dissolve.

The limit of uranium transport is determined by the final equilibrium between the transport salt and the acceptor alloy. Uranium transport stops when the equilibrium uranium content of the transport salt is the same above the donor and acceptor alloys.

Under the above conditions the system provides (1) control of magnesium buildup in the donor and (2) operation at optimum donor compositions. The optimum donor compositions provide maximum uranium solubility and the highest uranium distribution coefficient at the specified operating temperature during uranium salt transport.

The optimum initial bulk alloy composition is a function of the following: (1) desired uranium recovery, (2) ratio of liquid to solids in the donor, (3) operating temperature, (4) composition of the transport salt, (5) composition of the acceptor alloy, and (6) salt-to-metal ratio for bulk donor and acceptor alloys. For example, the initial bulk donor alloy composition [Cu-9.8 at. % Mg-5.3 at. % U (Cu-18.2 wt % U-3.5 wt % Mg)], point E on the ternary diagram (Fig. 5), is based on the following: (1) a uranium recovery of 99%, (2) an initial loading specified by a ratio of uranium in the eutectic to the total uranium of 0.20, (3) a temperature of 800°C, (4) MgCl_2 as the transport salt, (5) an acceptor alloy of the composition Zn-26.8 at. % Mg (Zn-12 wt % Mg), in which $D = 8.0 \times 10^{-3}$ for the uranium and all of it is in solution, and (6) a salt-to-metal weight ratio of 2 for both donor and acceptor alloys.

Temperature differences between the donor and acceptor alloys may be used to decrease the uranium content of the recycled transport salt. Additions of reagents such as copper or CuCl_2 may also be made to adjust the alloy composition.

B. Copper-Cadmium-Magnesium

The Cu-Cd-Mg ternary system was investigated as a potential donor alloy for a uranium salt-transport process. The objective of this

investigation was to determine whether it is possible to add cadmium to a Cu-Mg alloy to decrease the melting point and permit lower-temperature operation while at the same time retaining the favorable uranium donor properties of the Cu-Mg system.

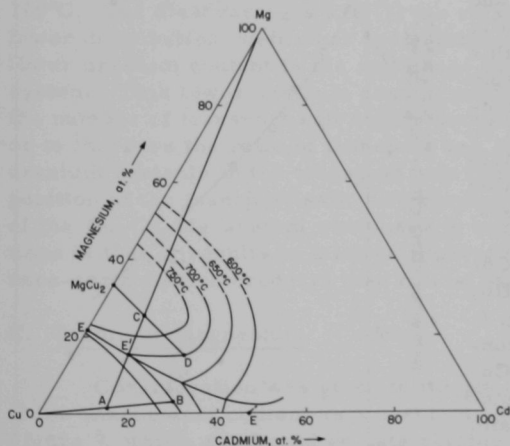


Fig. 6. Tentative Diagram of the Copper-rich Region of the Cu-Cd-Mg System

The results of thermal-analysis measurements together with existing data for the Cu-Cd and Cu-Mg binary systems were used to construct the tentative diagram in Fig. 6, which shows the liquidus isotherms at 600, 650, 700, and 750°C for the copper-rich region of the Cu-Cd-Mg system. Because of the location

of the isotherms and the relatively low boiling point of cadmium (767°C), the practical operating temperature is limited to a range between about 650 and 700°C.

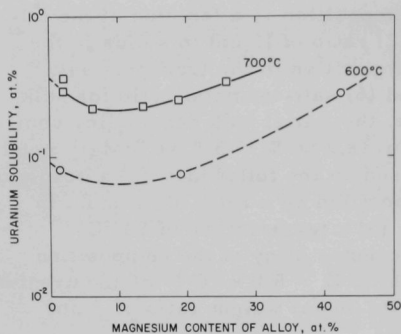


Fig. 7. Solubility of Uranium in Cu-40 at. % Cd-X at. % Mg Alloy at 600 and 700°C

30 mol % NaCl-20 mol % KCl (MgCl_2 -21.9 wt % NaCl-18.6 wt % KCl) salt phase at 700°C is shown as a function of magnesium content in the alloy in Fig. 8. In this case, the MgCl_2 , which has a melting point of 714°C, was diluted with NaCl and KCl to form a lower-melting salt phase (m.p. $\sim 396^\circ\text{C}$). With increasing magnesium content, the distribution coefficient of uranium decreases sharply, and it also appears to be essentially independent of temperature in this particular system. It is clear from the data in Fig. 8 that the magnesium content of the alloy must be kept rather low in order to maintain a high enough uranium distribution coefficient for a practical process.

The operation of the Cu-Cd-Mg system as a uranium donor alloy at 700°C is illustrated in Fig. 6. Line AEC lies on the tie line connecting the Cu-16.2 at. % Cd (Cu-25.5 wt % Cd) point with the magnesium corner of the ternary diagram. This segment of the tie line represents the path that the bulk composition of the alloy (on a uranium-free basis) will follow as uranium is transported out of the alloy and magnesium is added to the alloy through the reduction of MgCl_2 by

Figure 7 shows the effect of adding magnesium to a Cu-38.5 at. % Cd (Cu-52.5 wt % Cd) alloy on the solubility of uranium in the alloy at 600 and 700°C. At magnesium contents up to about 27 at. % (10 wt %), the uranium solubility at 700°C is in the general neighborhood of 0.28 at. % (1 wt %). This value is adequate, but not particularly favorable for a salt-transport process.

The uranium distribution coefficient between the same quasi-binary [Cu-38.5 at. % Cd-Mg (Cu-52.5 wt % Cd-Mg)] alloy system and a MgCl_2 -

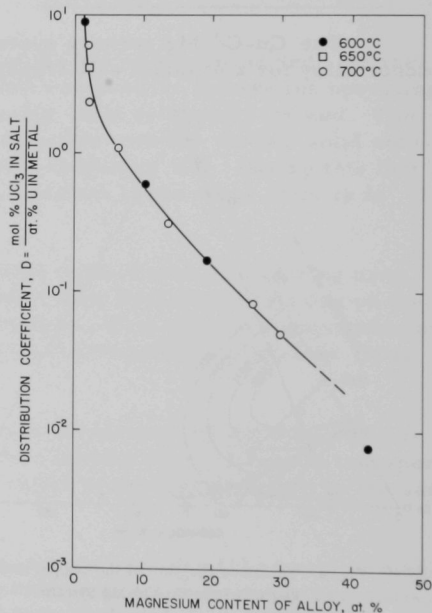


Fig. 8. Distribution of Uranium between MgCl_2 -30 mol % NaCl-20 mol % KCl Salt and Cu-40 at. % Cd-X at. % Mg Alloy

the uranium. Point A represents the initial bulk composition. One of the equilibrium solid phases at point A is Cu-Cd-Mg solid solution and the other is probably UCu_5 . The liquid phase that is present with the bulk composition at point A is of the composition represented by point B, which lies on the 700°C isotherm. As the magnesium content increases, the bulk composition of the alloy moves along line AE toward E and the Cu-Cd-Mg solid solution is dissolved. At the same time, the composition of the corresponding equilibrium liquid phase moves along the liquidus isotherm BE toward E. When the bulk composition reaches point E, all of the Cu-Cd-Mg solid solution is dissolved. As more magnesium is added, the compound MgCu_2 begins to form, and the composition of the liquid phase follows the liquidus isotherm on line ED toward point D. Under the conditions illustrated by this example, the bulk magnesium content can be increased from about 3.5 at. % (1.2 wt %) to 26.7 at. % (11 wt %) while the magnesium content of the liquid phase reaches a maximum value of only 17.4 at. % (6.0 wt %). With this system, 72 kg of uranium can be accommodated by 100 kg of initial donor alloy.

The Cu-Cd-Mg system has the following desirable features as a uranium donor alloy: (1) it provides a greater "buffering" action for control of magnesium than does the Cu-Mg system, with the result that a larger quantity of uranium can be accommodated by the same amount of donor alloy, and (2) the salt-transport operation can be carried out at 650-700°C. The disadvantages are (1) the volatility of cadmium, and (2) the lower distribution coefficient and solubility of uranium, which result in a lower uranium content in the salt phase than that obtained with the Cu-Mg system. This lower uranium content makes it necessary either to increase the number of transport salt cycles between the donor and acceptor alloys or to increase the ratio of transport salt to donor alloy. However, higher uranium contents in the transport salt can be obtained by changing the composition of the transport salt, as indicated in Sect. V. Another disadvantage of the Cu-Cd-Mg system when used in certain fuel reprocessing applications is that it results in a lower separation factor between plutonium and rare-earth fission products than can be obtained with the Cu-Mg system.

C. Cadmium-Magnesium

Consideration was given to the possibility of using a Cd-Mg alloy of low magnesium content as a uranium donor in a salt-transport process. Figure 9, which was based on data obtained by Martin,¹⁷ shows the effects of temperature and magnesium content on the solubility of uranium in Cd-Mg alloys. At low magnesium contents, the uranium solubility exhibits slightly retrograde behavior at temperatures above about 400-450°C. Since the uranium solubility decreases markedly with increasing magnesium content, the magnesium content of a Cd-Mg donor alloy must be kept low.

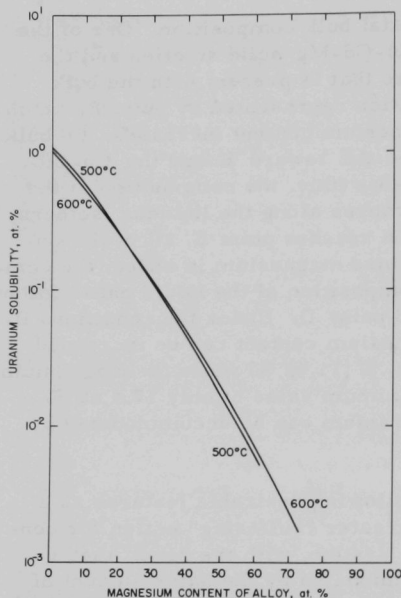


Fig. 9. Estimated Uranium Solubility in Cd-Mg Alloy (based on the data of Martin¹⁶)

Mg donor alloy at a low, constant value. To keep the magnesium content at a constant value, 0.153 kg of magnesium must be removed from the donor

The distribution coefficient of uranium between liquid Cd-Mg alloys and a MgCl_2 -30 mol % NaCl -20 mol % KCl (MgCl_2 -21.9 wt % NaCl -18.6 wt % KCl) salt phase at 600°C is shown as a function of magnesium content of the alloy in Fig. 10. The uranium distribution coefficient is not high enough in the Cd-Mg system for it to function as a satisfactory uranium donor alloy except at very low magnesium concentrations. The magnesium content of the donor alloy must be closely controlled because of the sensitivity of the distribution coefficient to small changes in magnesium content.

Unlike the Cu-Mg and Cu-Cd-Mg alloys, the Cd-Mg system does not provide the buffering effect that permits the magnesium content of the liquid alloy to be controlled by precipitating or dissolving solid inter-metallic phases. Therefore, some external method is required to maintain the magnesium content in the Cd-

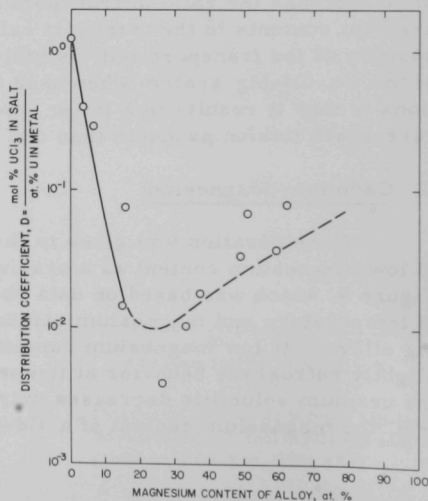


Fig. 10

Distribution of Uranium between MgCl_2 -30 mol % NaCl -20 mol % KCl Salt and Cd-Mg Alloy at 600°C

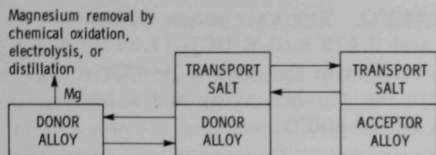


Fig. 11. Schematic Illustration of a Salt-transport Process with External Magnesium Control

include chemical oxidation, electrolysis, and distillation. In the case of a donor alloy such as Cd-Mg, distillation is undesirable because the major constituent, cadmium, is more volatile than the magnesium.

As a donor alloy, the Cd-Mg system is desirable because it can be used at a low temperature (down to about 500°C), and it can be contained in 400 series stainless steel equipment. However, the magnesium concentration must be controlled accurately by an external method, and the solubility of uranium is rather low.

D. Cadmium-Zinc-Magnesium

The Cd-Zn-Mg system is of interest as a uranium donor alloy because the uranium solubility and distribution coefficient are both large in certain composition regions. At 600°C a large peak in the solubility of uranium occurs at a cadmium-to-zinc weight ratio of about 9 to 1. Figure 12 shows estimated values of the uranium solubility as magnesium is added to an alloy of the initial composition Cd-15.2 at. % Zn (Cd-9.5 wt % Zn) at 600°C. The corresponding distribution coefficient of uranium between a Cd-15.2 at. % Zn (Cd-9.5 wt % Zn) alloy of varying magnesium content and a MgCl_2 -30 mol % NaCl-20 mol % KCl (MgCl_2 -21.9 wt % NaCl-18.6 wt % KCl) salt phase at 600°C is presented in Fig. 13. It is evident from Figs. 12 and 13 that the uranium solubilities and distribution coefficients are both large at low magnesium concentrations with a cadmium-to-zinc weight ratio of 9:1.

Figure 14 shows the results of uranium distribution coefficient measurements in a system consisting of a uranium-saturated Cd-15.9 at. % Zn-1.3 at. % Mg (Cd-9.97 wt % Zn-0.3 wt % Mg) liquid alloy and a MgCl_2 -30 mol % NaCl-20 mol % KCl (MgCl_2 -21.9 wt % NaCl-18.6 wt % KCl) molten salt that

alloy for every kilogram of uranium transported. Figure 11 illustrates schematically a salt-transport process in which external control of the magnesium concentration is accomplished by continuous removal of magnesium from a small side stream of the donor alloy. Possible techniques for magnesium removal

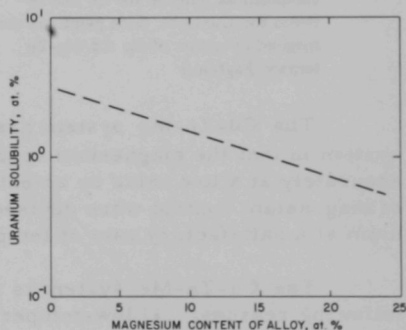


Fig. 12

Estimated Uranium Solubility in Cd-Zn-Mg Alloy at 600°C. (Alloy of compositions lying on the tie line between the Cd-15 at. % Zn point and the magnesium corner of the Cd-Mg-Zn ternary diagram)

was thermally cycled between 448 and 650°C. The salt phase contained 3.57 mol % UCl_3 (9.5 wt % U) at 650°C and 0.475 mol % UCl_3 (1.39 wt % U) at 448°C. In this system, the uranium content of the salt at 448°C is significantly greater than that obtained with the Cu-Mg alloy and a MgCl_2 salt phase [0.46 mol % UCl_3 (1.15 wt % U)] at 800°C.

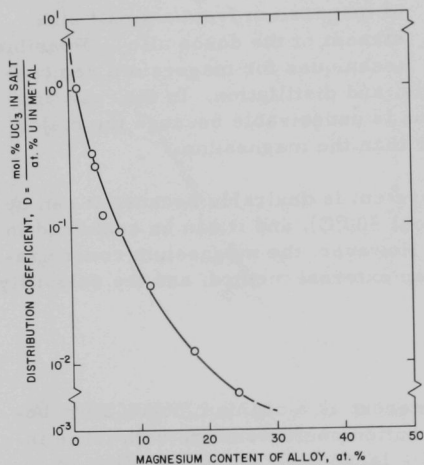


Fig. 13. Distribution of Uranium between MgCl_2 -30 mol % NaCl -20 mol % KCl Salt and Cd-Zn-Mg Alloy at 600°C. (Alloy of compositions lying on the tie line between the Cd-15 at. % Zn point and the magnesium corner of the Cd-Mg-Zn ternary diagram.)

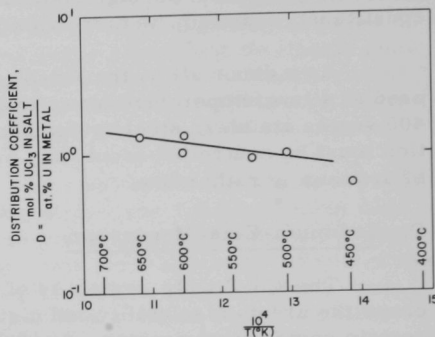


Fig. 14. Distribution of Uranium between MgCl_2 -30 mol % NaCl -20 mol % KCl Salt and Cd-15.85 at. % Zn-1.28 at. % Mg Alloy

The Cd-Zn-Mg system has the same disadvantage as the Cd-Mg system in that the magnesium concentration of the alloy must be controlled accurately at a low value by an external method. If a satisfactory method of magnesium control were devised, it should be possible to transfer uranium at a satisfactory rate at temperatures as low as 450°C.

The Cd-Zn-Mg system is a promising uranium donor alloy for the following reasons: (1) low-temperature (450-650°C) operation is possible; (2) it can be contained in series 400 stainless steels; (3) if any donor alloy reaches the acceptor alloy through entrainment, it can be removed from the product by retorting. The only important disadvantage is the problem of magnesium control.

IV. ACCEPTOR ALLOYS

The only systems that were investigated as acceptor alloys for a uranium salt-transport process were Zn-Mg and Cd-Mg. In order to remove the liquid metal solvent from the metallic uranium product by retorting (or vacuum distillation), the acceptor alloy must consist of relatively volatile metals. It is important to know the solubility of uranium in the acceptor alloy and the distribution coefficient of uranium between the alloy and the transport salt. These two factors determine the equilibrium uranium content in the recycle transport salt, which sets the minimum uranium loss in the donor alloy and in the transport salt. The acceptor alloy must be compatible with the donor alloy and the transport salt with respect to volatility, melting point, containment, density relationships, etc.

A. Zinc-Magnesium

The Zn-Mg system appears to offer the greatest promise as a uranium acceptor alloy. The solubility of uranium in the Zn-Mg system at temperatures of 600, 700, and 800°C is shown in Fig. 15. At these three temperatures maximum uranium solubility occurs at magnesium contents of 48.1, 37.4, and 27.4 at. % (24.8, 16.7, and 10.7 wt %), respectively. The corresponding solubilities of uranium at these three points are 0.89, 2.51, and 4.71 at. % (4.5, 11, and 18 wt %), respectively. Metallic uranium is the equilibrium solid phase on the magnesium side of the solubility peaks, and a series of U-Zn intermetallic compounds constitute the equilibrium solid phases on the zinc side.

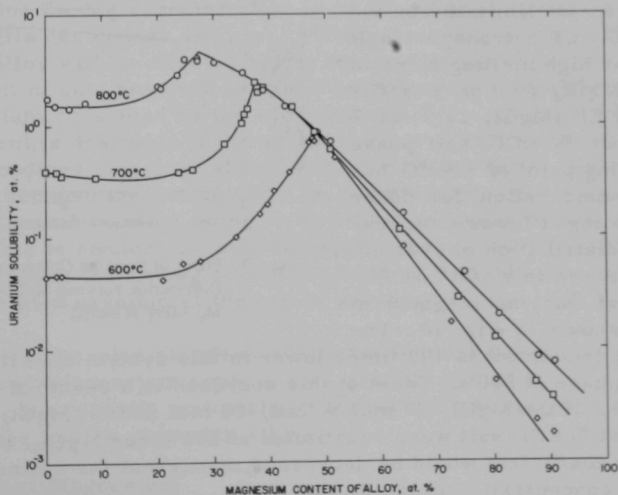


Fig. 15. Solubility of Uranium in Zn-Mg Alloy

Because MgCl_2 would most likely be used as a uranium transport salt with a Cu-Mg donor alloy, the distribution behavior of uranium between

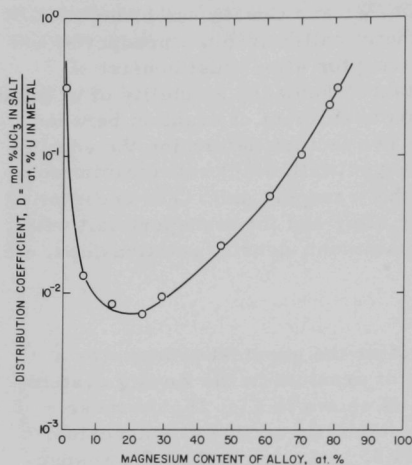


Fig. 16. Distribution of Uranium between MgCl_2 Salt and Zn-Mg Alloy at 800°C

been found to have an important effect on the uranium distribution coefficient in any of the investigations related to this work.

The major limitation on the use of MgCl_2 as a transport salt is its rather high melting point of 714°C . A MgCl_2 -30 mol % NaCl -20 mol % KCl (MgCl_2 -21.9 wt % NaCl -18.6 wt % KCl) salt phase with a melting point of $\sim 396^\circ\text{C}$ has received consideration for donor alloys operating at lower temperatures. The distribution of uranium at 600°C between this salt and Zn-Mg alloys of varying magnesium content is shown in Fig. 18. The distribution coefficient is 100 times lower in this system than it is with a MgCl_2 salt phase at 800°C . Most of this decrease is a result of the lower temperature. If the MgCl_2 -30 mol % NaCl -20 mol % KCl (MgCl_2 -21.9 wt % NaCl -18.6 wt % KCl) salt were substituted at 800°C for MgCl_2 , the uranium distribution coefficient would be decreased throughout the entire range of magnesium concentration in the Zn-Mg alloy.

a Zn-Mg acceptor alloy of varying magnesium content and MgCl_2 at 800°C was determined. The results appear in Fig. 16. A pronounced minimum in the distribution coefficient curve occurs at about 23 at. % (10 wt %) magnesium. However, because of the combined effects of uranium solubility, distribution, and the equilibrium solid phase involved, it is desirable to use an acceptor alloy of higher magnesium content [73 at. % (~ 50 wt %)]. These effects will be discussed later.

The effect of uranium concentration on uranium distribution between a Zn-23 at. % Mg (Zn-10 wt % Mg) alloy and MgCl_2 proved to be small as shown by the data in Fig. 17. The concentration of uranium in liquid metal alloys has not

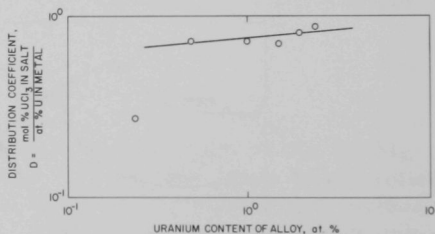


Fig. 17. Effect of Uranium Content upon Uranium Distribution between MgCl_2 Salt and Zn-Mg Alloy at 800°C

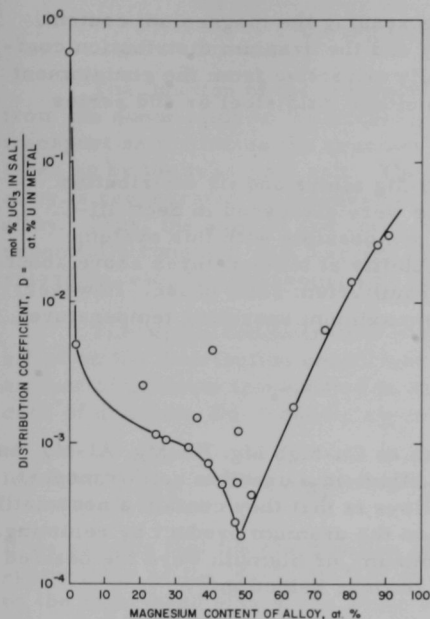


Fig. 18. Distribution of Uranium between MgCl_2 -30 mol % NaCl -20 mol % KCl Salt and Uranium-saturated Zn-Mg Alloy at 600°C

When large amounts of uranium are to be accommodated by the acceptor alloy, it should have a sufficiently high magnesium content so that metallic uranium, rather than uranium-zinc intermetallic compounds, is the equilibrium solid phase. This will prevent zinc from being removed from the acceptor alloy by precipitation of the intermetallic compounds. Since uranium has a low solubility in Zn-Mg acceptor alloys of high magnesium content, its solubility limit is reached early in the salt-transport operation. As additional uranium is introduced into the alloy, it precipitates as uranium metal. The only significant change in the liquid alloy composition results from the magnesium consumed by the reduction of UCl_3 . At high magnesium contents, the solubility of uranium and the uranium distribution coefficient are not affected significantly by changes in the magnesium content of the Zn-Mg acceptor alloy.

If the Zn-Mg acceptor alloy is of a composition such that U-Zn intermetallic compounds are precipitated, the composition of the liquid acceptor alloy will be affected by the removal of zinc from the solution. The amount of zinc removed by this mechanism far outweighs the quantity of magnesium consumed by the reduction of UCl_3 . Although a high magnesium content is desirable if the acceptor alloy is to accommodate large uranium loadings, acceptor alloys with lower magnesium contents are attractive because the uranium can be removed from the acceptor vessel as a liquid metal solution owing to its higher solubility in zinc-rich alloys. It is possible to conduct the salt-transport operation with a high magnesium concentration in the Zn-Mg acceptor alloy and then add zinc to solubilize the precipitated uranium at the end of the operation.

The 400 series stainless steels can be used to contain Zn-Mg alloys of high magnesium content, i.e., greater than about 70 at. % (~50 wt %), but ceramic materials or metals such as tungsten or molybdenum are required for the zinc-rich alloys.

B. Cadmium-Magnesium

The Cd-low Mg system was mentioned in Sect. III-C as a potential donor alloy in a uranium salt-transport process. A Cd-Mg system may

also be used as an acceptor alloy by increasing the magnesium content, which decreases the uranium solubility and the uranium distribution coefficient. The Cd-Mg system is especially attractive from the containment standpoint, since it is not corrosive to either mild steel or 400 series stainless steels.

The solubility of uranium in Cd-Mg alloys and its distribution behavior between these alloys and salts were discussed in Sect. III-C. High loadings of precipitated uranium are possible with this system because of the retrograde uranium solubility at temperatures above about 450°C, where metallic uranium is the equilibrium solid phase. However, the volatility of cadmium restricts the maximum operating temperature to about 700°C.

C. Other Acceptor Alloys

Other alloys of magnesium such as Cu-high Mg, Pb-Mg, Al-Mg, and Bi-Mg could also be used as acceptor alloys in a uranium salt-transport process. The disadvantage of these alloys is that they contain a nonvolatile constituent that cannot be removed from the uranium product by retorting. If uranium alloys of copper, lead, aluminum, or bismuth were the desired product, these acceptors would be the obvious selection.

V. TRANSPORT SALTS

The function of the transport salt is to carry the uranium, as UCl_3 , from the donor alloy to the acceptor alloy. Magnesium chloride in the transport salt oxidizes the uranium in the donor alloy to UCl_3 , which is taken up by the transport salt. The MgCl_2 that is consumed at the donor alloy is regenerated by magnesium reduction of UCl_3 at the acceptor alloy. Thus, the amount and composition of the transport salt remain essentially constant, and, barring process losses through vaporization, splashing, etc., the transport salt can be used indefinitely.

The MgCl_2 concentration in the transport salt has an important effect on the distribution coefficient of uranium, which in turn affects the amount of uranium transported in each cycle of the transport salt. For the case of uranium, Eq. 5 can be expressed as follows:

$$\log D = \frac{\Delta G^\circ}{2.3RT} - \frac{3}{2} \log a_{\text{Mg}} + \log \gamma_{\text{U}} + \frac{3}{2} \log a_{\text{MgCl}_2} - \log \gamma_{\text{UCl}_3} \quad (21)$$

If we assume that the composition of the metal phase does not change appreciably as the MgCl_2 content of a salt is varied, the first three terms on the right-hand side of the above expression remain essentially constant. If $\log C$ is substituted for these three terms, and a_{MgCl_2} is expressed as $x_{\text{MgCl}_2} \gamma_{\text{MgCl}_2}$, this expression becomes

$$\log D = \log C + \log \left[\frac{\gamma_{\text{MgCl}_2}^{3/2}}{\gamma_{\text{UCl}_3}} \right] + \frac{3}{2} \log x_{\text{MgCl}_2} \quad (22)$$

Little information is available on the values of γ_{MgCl_2} and γ_{UCl_3} for the salt systems used in these investigations. If the ratio in the brackets does not change markedly, the distribution coefficient will be proportional to the three-halves power of the atom fraction of MgCl_2 in the salt.

Figure 19 shows experimental data on the distribution of uranium at 800°C between a Cu-15.8 at. % Mg-1.03 at. % U (Cu-6.4 wt % Mg-4.15 wt % U) alloy saturated with uranium and salt consisting of equimolar NaCl-CaCl₂ with varying amounts of MgCl_2 . The experimental points can be correlated reasonably well with the curve, which is represented by the expression

$$D = 0.385(x_{\text{MgCl}_2})^{3/2} \quad (23)$$

The observed dependence on the three-halves power of x_{MgCl_2} may be fortuitous, inasmuch as the ratio shown in brackets in Eq. 22 remains nearly constant. Although Eq. 23 cannot be completely justified on a theoretical basis, it has proved to be a useful empirical correlation.

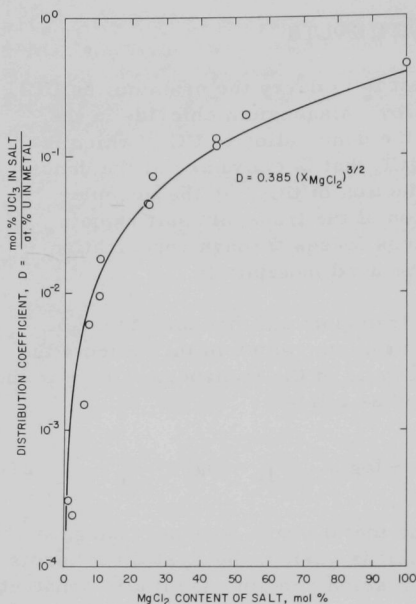


Fig. 19. Distribution of Uranium between NaCl-50 mol % CaCl_2 -X mol % MgCl_2 Salt and Cu-15.8 at. % Mg-1.03 at. % U Alloy at 800°C

The data in Fig. 19 show that the distribution coefficient of uranium increases by a factor of 10^3 when the MgCl_2 content of the salt is increased from 1 to 100 mol %. Thus, for maximum efficiency of uranium transfer, it is desirable to use the highest MgCl_2 concentration that is compatible with the other requirements of the operation.

Most of the experimental work employed MgCl_2 -based salts. At temperatures above 750°C, undiluted MgCl_2 proved to be a satisfactory uranium transport salt. Although MgCl_2 -30 mol % NaCl-20 mol % KCl (MgCl_2 -21.9 wt % NaCl-18.6 wt % KCl) was used in most of the work at lower temperatures (600-700°C), it is not necessarily the optimum composition for this purpose. Depending on the melting point requirement, other combinations of MgCl_2 and alkali or alkaline earth chlorides may be more favorable.

Salts containing magnesium halides other than MgCl_2 deserve consideration for a uranium salt-transport process. Little attention has been given to all-fluoride systems because of their higher melting points and larger free energies of formation, but the MgCl_2 -22 mol % MgF_2 (MgCl_2 -15.6 wt % MgF_2) eutectic (m.p. 626°C) appears attractive. Bromide systems offer more favorable uranium distribution coefficients than do the corresponding chlorides. For example, the distribution coefficient is more than doubled when MgBr_2 -30 mol % NaBr-20 mol % KBr is substituted for the analogous chloride system. Although the process might be improved significantly by the use of halide salts other than the chlorides or by appropriate mixed halide systems, little work has been done in this area.

VI. DISCUSSION

The transfer of uranium from the donor to the acceptor alloy will continue as long as the uranium concentration of the transport salt in contact with the donor alloy is greater than the uranium concentration in the transport salt in contact with the acceptor alloy. The equilibrium uranium concentration in the transport salt is equal to the product of the distribution coefficient and the uranium content of the liquid alloy. The

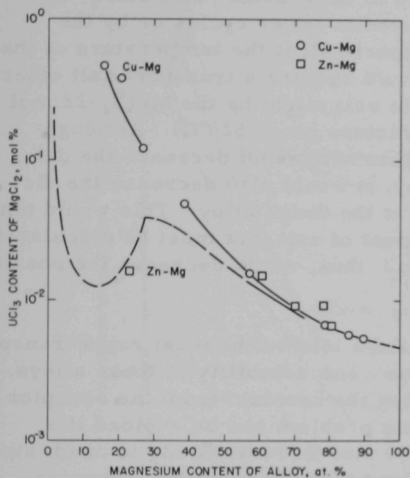


Fig. 20. Uranium Trichloride Content of $MgCl_2$ Salt in Equilibrium with Uranium-saturated Cu-Mg and Zn-Mg Alloys at 800°C

maximum concentrations of uranium in molten $MgCl_2$ in equilibrium with liquid Cu-Mg and Zn-Mg alloys are obtained when the alloys are saturated with uranium, as illustrated in Fig. 20. Under these conditions, the largest difference of uranium concentrations in the transport salt (optimum conditions for salt transport) would occur when the transport salt is in contact with a Cu-Mg donor alloy with the lowest magnesium content and a Zn-Mg acceptor alloy with the highest magnesium content. Molten magnesium might be used as an acceptor alloy if the technical problems associated with the use of a metal phase that is less dense than the transport salt could be readily solved. However, Fig. 20 shows that the addition of up to 30 at. % (52 wt %) zinc to magnesium to increase the density of the alloy would increase the maximum uranium

content of the transport salt by less than a factor of two. The optimum Cu-Mg donor alloy for uranium transport has a composition that lies on the eutectic valley in the Cu-Mg-U system (point C in Fig. 5) at the operating temperature. The magnesium content of this donor alloy may be maintained at this low value by the buffering action provided by the dissolution and precipitation of solid intermetallic phases as discussed in Sect. III.

The rate of salt transport of uranium with a Cu-Mg donor alloy may be improved if the temperature is increased. An increase in temperature allows a liquid alloy with a lower magnesium content to be used, which, in turn, leads to a greater uranium solubility and a larger value for the distribution coefficient for uranium. The substitution of bromide for chloride in the transport salt would also increase the rate of the salt transport of uranium by increasing the value of the distribution coefficient.

The rate of uranium salt transport may be increased if the rate of back transfer of uranium from the acceptor to the donor alloy is decreased. The back transfer of uranium may be decreased by lowering the uranium content of the transport salt recycled from the acceptor alloy. The Zn-high Mg acceptor alloy becomes saturated with uranium after a small fraction of the uranium has been transferred. The uranium content of the recycled transport salt is then constant and equal to the product of the distribution coefficient and the solubility. Both the distribution coefficient and the solubility are lowered if the temperature is decreased. Therefore, the salt transport of uranium could be achieved in fewer cycles or by the circulation of a smaller amount of transport salt if the temperature of the acceptor alloy were decreased. This would require a transport salt other than pure MgCl_2 (m.p. 714°C). A suitable salt might be the MgCl_2 -22 mol % MgF_2 (MgCl_2 -15.6 wt % MgF_2) eutectic mixture (m.p. 626°C). Although lowering the MgCl_2 content of the transport salt would decrease the distribution coefficient at the acceptor alloy, it would also decrease the distribution coefficient by the same factor at the donor alloy. This would tend to increase the number of cycles or amount of salt that must be circulated to achieve the same uranium transfer and, thus, would decrease the possible decontamination.

The high-magnesium acceptor alloys lead to the most rapid transport of uranium. However, since uranium has a low solubility in these alloys, difficulty may be encountered in removing the uranium from the acceptor alloy vessel for further processing. This problem can be avoided if a Zn-Mg acceptor alloy containing about 30 mol % (14 wt %) Mg is used, since the uranium solubility in this alloy is about 4 at. % (15 wt %). However, Fig. 20 shows that the uranium content of the transport salt would be about six times greater when saturation of the acceptor alloy is achieved. If, however, the concentration in the acceptor alloy is not permitted to reach saturation, comparable uranium transfers may be achieved by the circulation of approximately the same amount of transport salt.

Several other donor alloys were investigated in an attempt to avoid the problems associated with operating at temperatures above 800°C , or operating with the donor and acceptor alloys at different temperatures. The uranium content of MgCl_2 -30 mol % NaCl -20 mol % KCl (MgCl_2 -21.9 wt % NaCl -18.6 wt % KCl) salt in contact with uranium-saturated Cd-Cu-Mg, Cd-Mg, Cd-Zn-Mg, and Zn-Mg alloys is shown in Fig. 21. It can be seen that it is possible to use donor alloys at temperatures lower than 800°C provided the problems associated with maintaining the necessary low magnesium contents can be solved. The Cu-Cd-Mg alloy system is probably the most promising one.

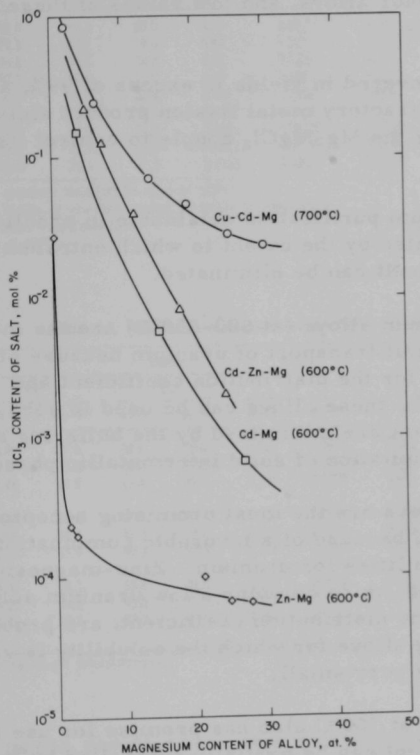


Fig. 21

UCl_3 Content of MgCl_2 -30 mol %
 NaCl -20 mol % KCl Salt in Equi-
 librium with Uranium-saturated
 Magnesium Alloys

VII. SUMMARY AND CONCLUSIONS

1. The factors that are important in choosing the donor and acceptor alloys and a transport salt are (a) the distribution coefficient of the metal to be transferred in the transport salt-alloy systems and (b) the solubility of the metal in the alloys. High values of the distribution coefficients and solubilities are desirable for donor alloys, and low values of these quantities are desirable for acceptor alloys.
2. Uranium can be recovered in yields in excess of 99%, and separated from the noble and refractory metal fission product elements by the salt-transport process using the Mg-MgCl₂ couple to control its distribution coefficient.
3. The degree of uranium purification obtainable in practical systems will most likely be limited by the extent to which entrainment of the donor alloy in the transport salt can be eliminated.
4. Copper-low magnesium alloys (at 800-850°C) are the most promising donor alloys for the salt transport of uranium because of a favorable combination of values for the distribution coefficient and solubility of uranium. In addition, these alloys can be used in such a way that changes in magnesium content are minimized by the buffering action afforded by dissolution and precipitation of solid intermetallic phases.
5. Zinc-magnesium alloys are the most promising acceptor alloys for the salt transport of uranium because of a favorable combination of distribution coefficient and solubilities for uranium. Zinc-magnesium alloys of high magnesium content, which combine a low uranium solubility with moderately high values of the distribution coefficient, are probably somewhat better than Zn-low Mg alloys for which the solubility is greater but the distribution coefficient is very small.
6. The Cu-Cd-Mg alloy at 700°C also has promise for use as a donor alloy; the magnesium content can be partially controlled by the buffering action afforded by the dissolution and precipitation of intermetallic phases.
7. The necessity for external control of the magnesium content at low values for Cd-Mg and Cd-Zn-Mg alloys limits the usefulness of these systems as donor alloys for uranium.
8. In the all-chloride transport salt, the highest possible concentrations of MgCl₂ are desirable for rapid uranium transport.
9. Magnesium bromide and MgI₂ are potentially useful transport salts for uranium. The MgCl₂-22 mol % MgF₂ (MgCl₂-15.6 wt % MgF₂) eutectic mixture (m.p. 626°C) can be used for lower-temperature operation.

APPENDIX

TABLE A-1. Distribution of Uranium between $MgCl_2$ Salt and Uranium-saturated Cu-Mg Alloy at 800°C

Metal						Salt		Distribution Coefficient	
Mg		Cu		U					
wt %	at. %	wt %	at. %	wt % ^a	at. % ^a	U, wt % ^b	UCl ₃ , mol % ^b	K _d , wt %/wt %	D, mol %/at. %
6.55 ^c	15.9	89.3	83.0	4.17	1.04	1.15	0.466	0.28 (avg 0.29) ^d	0.45
8.92	20.8	87.7	78.4	3.42	0.816	0.93	0.376	0.27	0.46
12.1	26.8	85.7	72.7	2.25	0.510	0.30	0.120	0.13	0.24
19.3	38.7	79.8	61.2	0.91	0.186	0.122	0.0489	0.13	0.26
33.7	57.1	66.1	42.9	0.177	0.0306	0.039	0.0156	0.22	0.51
46.7	69.6	53.2	30.4	0.0753	0.0115				
58.5	78.7	41.5	21.3	0.0543	0.00746	0.0169	0.00676	0.29	0.91
68.8	85.2	31.2	14.8	0.0407	0.00515	0.0143	0.00572	0.35	1.1
76.6	89.5	23.4	10.5	0.0338	0.00404	0.0135	0.00540	0.40	1.3

^aRepresents uranium solubility in alloy at 800°C.^bRepresents maximum uranium content in $MgCl_2$ at equilibrium.^cThis point taken from Table A-2.^dAverage K_d at 800°C.TABLE A-2. Distribution of Uranium between $MgCl_2$ Salt and Cu-Mg Alloys at 750, 800, and 850°C

Temp (°C)	Metal						Salt		Distribution Coefficient	
	Mg		Cu		U					
	wt %	at. %	wt %	at. %	wt %	at. %	U, wt %	UCl ₃ , mol %	K _d , wt %/wt %	D, mol %/at. %
750	8.49	19.6	91.4	80.4	0.160	0.0376	0.305	0.0140	0.22	0.37
750	8.57	19.8	90.6	80.0	0.800	0.189	0.199	0.0798	0.25	0.42
750	8.48	19.8	87.4	79.7	2.10 ^a	0.500 ^a	0.417	0.168	0.20	0.34
									(Average = 0.22)	(Average = 0.38)
800	7.06	16.6	92.8	83.4	0.117	0.0281	0.0337	0.0135	0.29	0.48
800	6.96	16.4	92.5	83.4	0.610	0.147	0.185	0.0742	0.30	0.51
800	6.55	15.9	89.3	83.0	4.17 ^a	1.04 ^a	1.15	0.466	0.28	0.45
									(Average = 0.29)	(Average = 0.48)
850	6.36	15.1	93.6	84.9	0.093	0.0225	0.040	0.0160	0.43	0.71
850	6.10	14.6	93.5	85.3	0.490	0.120	0.204	0.0818	0.42	0.69
850	4.76	12.2	87.7	85.9	7.55 ^a	1.97 ^a	3.05	1.26	0.40	0.64
									(Average = 0.42)	(Average = 0.68)

^aBelieved to represent solubility limit.TABLE A-3. Distribution of Uranium between 50 mol % $MgCl_2$ -30 mol % $NaCl$ -20 mol % KCl Salt and Mg-Cd-Cu Alloy

No.	Temp (°C)	Metal								Salt		Distribution Coefficient	
		Mg		Cd		Cu		U					
		wt %	at. %	wt %	at. %	wt %	at. %	wt %	at. %	U, wt %	UCl ₃ , mol %	K _d , wt %/wt %	D, mol %/at. %
1	600	0.39	1.34	54.8	40.5	44.5	58.1	0.23	0.0802	1.93	0.714	8.4	8.9
2	600	3.08	10.4	61.5	44.7	34.8	44.8	0.067	0.023	0.039	0.0137	0.58	0.60
3	600	6.13	19.2	59.7	40.5	33.4	40.0	0.236	0.0756	0.036	0.0127	0.15	0.17
4	600	17.9	42.4	38.2	19.6	41.2	37.3	1.17	0.283	0.007	0.00246	0.0060	0.0087
5	650	0.62	2.05	50.1	35.9	48.8	61.9	0.310	0.105	1.19	0.433	3.8	4.1
6	700	0.62	2.02	45.7	32.3	52.3	65.3	1.09	0.363	2.28	0.844	2.1	2.3
7	700	0.58	1.95	51.7	37.6	46.7	60.1	0.860	0.295	4.62	1.77	5.4	6.0
8	700	1.93	6.28	50.8	35.8	46.3	57.6	0.670	0.223	0.680	0.242	1.0	1.1
9	700	4.39	13.6	49.3	33.1	44.5	52.8	0.716	0.227	0.200	0.0705	0.28	0.31
10	700	6.36	19.0	49.7	32.1	42.5	48.5	0.840	0.256	0.130	0.0458	0.16	0.18
11	700	9.18	25.8	47.0	28.6	41.8	45.0	1.18	0.339	0.0800	0.0282	0.068	0.083
12	700	11.1	29.8	42.8	24.9	43.4	44.6	1.70	0.466	0.0660	0.0233	0.039	0.050

TABLE A-4. Distribution of Uranium between 50 mol % MgCl_2 -30 mol % NaCl -20 mol % KCl Salt and Mg - Cd Alloy at 600°C

TABLE A-4. Distribution of Uranium between 50 mol % MgCl ₂ -50 mol % UO ₂ and 50 mol % CdCl ₂ -50 mol % UO ₂									
Metal						Salt		Distribution Coefficient	
Mg		Cd		U					
wt %	at. %	wt %	at. %	wt %	at. %	U, wt %	UCl ₃ , mol %	K _d , wt %/wt %	D, mol %/at. %
0.03	0.13	100	99.9	0.00110	0.000519	0.0190	0.00643	0.17	0.12
0.80	3.60		98.4	96.0	0.820	0.378	0.440	0.54	0.40
3.60	14.8		95.4	84.8	0.940	0.394	0.0170	0.00574	0.018
7.14	26.3		92.3	73.5	0.460	0.173	0.00200	0.000674	0.0044
11.4	37.4		88.2	62.5	0.196	0.0655	0.00350	0.00118	0.018
17.1	48.8		82.7	51.1	0.0850	0.0248	0.00250	0.000843	0.029
23.8	59.1		76.1	40.9	0.0336	0.00852	0.000940	0.000317	0.028

TABLE A-5. Distribution of Uranium between 50 mol % MgCl_2 -30 mol % NaCl -20 mol % KCl Salt and Mg - Cd Alloy

Temp (°C)	Metal						Salt		Distribution Coefficient	
	Mg		Cd		U					
	wt %	at. %	wt %	at. %	wt %	at. %	U, wt %	UCl ₃ , mol %	K _d , wt %/wt %	D, mol %/at. %
425	1.43	6.33	97.3	93.1	0.738	0.333	0.0157	0.00528	0.021	0.016
425	4.11	16.7	94.5	82.8	0.828	0.343	0.0282	0.00949	0.034	0.028
425	10.2	34.6	88.8	65.1	0.149	0.0516	0.00806	0.00271	0.054	0.053
425	18.1	50.7	81.1	49.1	0.0288	0.00823	0.0133	0.00447	0.46	0.54
500	1.29	5.76	96.5	93.2	1.45	0.662	0.0889	0.0300	0.061	0.045
500	3.97	16.2	94.5	83.2	0.742	0.309	0.0169	0.00569	0.023	0.018
500	9.65	33.2	89.4	66.5	0.150	0.0534	0.0261	0.00879	0.17	0.17
500	18.3	51.0	80.9	48.8	0.0330	0.00939	0.00787	0.00265	0.24	0.28
500	25.4	61.3	74.0	38.6	0.0178	0.00439	0.0120	0.00404	0.67	0.92
600	1.50	6.64	96.7	92.6	0.977	0.442	0.376	0.127	0.39	0.29
600	3.92	16.0	94.6	83.4	0.695	0.289	0.0642	0.0216	0.092	0.075
600	9.67	33.2	89.3	66.4	0.231	0.0811	0.00249	0.000838	0.011	0.010
600	18.2	50.8	81.0	48.9	0.0597	0.0170	0.00347	0.00117	0.058	0.069
600	26.1	62.1	73.2	37.7	0.0288	0.00700	0.00164	0.000552	0.057	0.079

TABLE A-6. Distribution of Uranium between 50 mol % MgCl_2 -30 mol % NaCl -20 mol % KCl Salt and Mg - Zn - Cd Alloy^a at 600°C

No.	Metal								Salt		Distribution Coefficient	
	Mg		Zn		Cd		U					
	wt %	at. %	wt %	at. %	wt %	at. %	wt %	at. %	U, wt %	UCl ₃ , mol %	K _d , wt %/wt %	D, Mol %/at. %
1	0.74	3.38	0.00	0.0	96.3	95.2	0.930	0.434	0.424	0.148	0.46	0.34
2	0.79	3.62	0.00	0.0	95.4	94.6	1.01	0.473	0.380	0.132	0.38	0.28
3	1.08	4.67	9.33	15.0	82.6	77.2	3.97	1.75	0.620	0.214	0.16	0.12
4	1.68	7.12	9.14	14.4	82.4	75.5	3.13	1.35	0.364	0.125	0.12	0.092
5	2.82	11.5	9.08	13.8	81.5	71.9	2.57	1.07	0.116	0.0395	0.045	0.037
6	4.65	17.9	8.90	12.7	80.7	67.1	1.72	0.676	0.0240	0.00813	0.014	0.012
7	6.70	24.2	8.76	11.8	79.1	61.9	0.910	0.336	0.00600	0.00203	0.0066	0.0060

^aAlloy composition lies on the line between the Cd -15 at. % Zn binary and the magnesium corner of the Mg - Zn - Cd ternary alloy.TABLE A-7. Distribution of Uranium between 50 mol % MgCl_2 -30 mol % NaCl -20 mol % KCl Salt and Cd -9.5 at. % Zn -0.25 at. % Mg Alloy

Temp (°C)	Metal								Salt		Distribution Coefficient	
	Mg		Zn		Cd		U					
	wt %	at. %	wt %	at. %	wt %	at. %	wt %	at. %	U, wt %	UCl ₃ , mol %	K _d , wt %/wt %	D, mol %/at. %
448	0.16	0.69	9.81	15.8	88.3	82.7	1.76	0.779	1.39	0.475	0.79	0.61
500	0.23	1.01	9.57	15.6	86.2	81.6	4.03	1.80	5.10	1.82	1.3	1.0
530	0.25	1.10	9.51	15.5	85.6	81.3	4.61	2.07	5.40	1.93	1.2	0.93
598	0.23	1.00	9.70	15.7	87.3	82.1	2.80	1.24	4.72	1.68	1.7	1.4
600	0.28	1.21	9.71	15.7	87.4	82.0	2.64	1.17	3.41	1.19	1.3	1.0
650	0.36	1.59	9.37	15.4	84.4	80.4	5.91	2.66	9.50	3.57	1.6	1.3

TABLE A-8. Solubility of Uranium in Zn-Mg Alloy at 700°C and 800°C

700°C						800°C					
Mg		Zn		U		Mg		Zn		U	
wt %	at. %	wt %	at. %	wt %	at. %	wt %	at. %	wt %	at. %	wt %	at. %
0.03	0.08	98.5	99.5	1.43	0.397	0.11	0.31	93.8	98.0	6.07	1.74
0.65	1.74	97.9	97.9	1.41	0.387	0.60	1.66	94.1	96.8	5.33	1.51
1.00	2.67	97.7	97.0	1.33	0.363	1.53	4.16	93.3	94.4	5.17	1.44
3.40	8.72	95.3	90.9	1.30	0.341	2.64	7.08	91.5	91.3	5.84	1.60
10.2	23.6	88.2	76.0	1.60	0.379	8.22	20.5	83.3	77.3	8.53	2.18
11.5	26.2	86.7	73.4	1.73	0.402	7.99	20.0	83.3	77.7	8.70	2.23
14.5	31.9	82.5	67.5	3.00	0.674	9.44	23.5	79.5	73.7	11.1	2.83
16.1	35.0	79.2	64.0	4.70	1.04	9.68	24.7	75.2	71.4	15.1	3.93
16.1	35.3	78.2	63.5	5.66	1.26	10.7	27.1	73.6	68.9	15.7	4.04
16.5	36.0	77.2	62.6	6.30	1.40	10.8	27.1	74.2	69.1	15.0	3.84
17.7	37.3	72.6	60.3	10.7	2.44	12.3	30.0	72.8	66.2	14.9	3.72
17.3	37.8	73.9	60.2	8.80	1.97	15.3	35.2	72.0	61.8	12.7	2.99
17.8	38.8	72.7	59.1	9.60	2.14	17.8	38.9	72.8	59.0	9.4	2.09
21.4	43.9	71.7	54.6	6.92	1.45	20.6	42.8	72.4	55.8	7.00	1.48
24.8	48.0	70.9	51.1	4.39	0.870	17.1	50.9	69.3	48.4	3.69	0.71
27.1	50.8	69.8	48.7	3.11	0.595	39.5	64.0	59.5	35.9	9.70	0.16
38.7	63.1	60.6	37.8	0.69	0.115	51.2	74.8	45.7	24.8	3.13	0.047
50.7	73.5	49.1	26.5	0.190	0.028	60.8	80.7	39.1	19.3	1.44	0.020
59.9	80.1	40.0	19.9	0.091	0.012	72.9	87.9	27.1	12.1	6.70	0.0083
72.8	87.8	27.1	12.2	0.04	0.0049	78.1	90.6	21.8	9.40	6.29	0.0075
77.6	90.3	22.4	9.70	0.031	0.0037						

TABLE A-9. Distribution of Uranium between $MgCl_2$ Salt and Zn-Mg Alloy at 800°C

Metal						Salt		Distribution Coefficient	
Mg		Zn		U		U, wt %	UCl_3 , mol %	K_d , wt %/wt %	D, mol %/at. %
wt %	at. %	wt %	at. %	wt %	at. %				
0.23	0.63	96.5	98.5	3.29	0.922	0.720	0.290	0.22	0.32
2.22	5.92	93.7	93.0	4.08	1.11	0.0373	0.0149	0.0091	0.013
5.71	14.4	90.4	84.6	3.92	1.01	0.0212	0.00848	0.0054	0.0084
9.73	23.4	84.2	75.2	6.03	1.48	0.0261	0.0104	0.0043	0.0071
12.9	29.1	83.7	70.2	3.40	0.783	0.0184	0.00736	0.0054	0.0094
23.8	46.5	72.7	52.8	3.54	0.706	0.0390	0.0156	0.011	0.022
35.9	60.6	62.4	39.1	1.72	0.296	0.0374	0.0150	0.022	0.051
46.0	69.8	53.4	30.1	0.580	0.0899	0.0230	0.00920	0.040	0.10
56.6	77.9	43.1	22.1	0.284	0.0399	0.0236	0.00944	0.083	0.24
60.0	80.2	39.9	19.8	0.155	0.0212	0.0165	0.00660	0.11	0.31

TABLE A-10. Effect of Uranium Content upon Uranium Distribution between $MgCl_2$ Salt and Zn-23 at. % Mg Alloy at 800°C

Metal						Salt		Distribution Coefficient	
Mg		Zn		U		U, wt %	UCl_3 , mol %	K_d , wt %/wt %	D, mol %/at. %
wt %	at. %	wt %	at. %	wt %	at. %				
10.3	23.7	88.7	76.1	1.00	0.236	0.00160	0.000640	0.0016	0.0027
10.1	23.5	87.8	76.0	2.04	0.485	0.00880	0.00352	0.0043	0.0073
9.90	23.4	86.0	75.6	4.11	0.992	0.0181	0.00724	0.0044	0.0073
9.73	23.4	84.2	75.2	6.03	1.48	0.0261	0.0104	0.0043	0.0071
9.47	23.1	82.8	75.0	7.76	1.93	0.0394	0.0158	0.0051	0.0082
9.18	22.7	81.5	75.0	9.32	2.35	0.0520	0.0208	0.0056	0.0088

TABLE A-11. Distribution of Uranium between 50 mol % MgCl₂-30 mol % NaCl-20 mol % KCl Salt and Uranium-saturated Zn-Mg Alloy at 600°C

Metal						Salt		Distribution Coefficient	
Mg		Zn		U		U, wt %	UCl ₃ , mol %	K _d , wt %/wt %	D, mol %/at. %
wt %	at. %	wt %	at. %	wt %	at. %				
0.03	0.08	99.8	99.9	0.162	0.0445	0.0790	0.0266	0.49	0.60
0.72	1.92	99.1	98.0	0.170	0.0462	0.000690	0.000232	0.0041	0.0050
1.03	2.73	98.8	97.2	0.170	0.0459	0.000600	0.000202	0.0035	0.0044
8.88	20.8	90.9	79.2	0.176	0.0421	0.000320	0.000108	0.0018	0.0026
10.8	24.5	89.0	75.4	0.250	0.0582	0.000199	0.0000669	0.00080	0.0012
12.4	27.6	87.4	72.4	0.270	0.0614	0.000197	0.0000663	0.00073	0.0011
16.0	34.0	83.5	65.9	0.462	0.100	0.000280	0.0000942	0.00061	0.00094
18.5	38.1	80.7	61.7	0.760	0.160	0.000720	0.000242	0.00095	0.0015
19.5	39.6	79.6	60.2	0.940	0.195	0.000484	0.000163	0.00052	0.00083
21.9	43.5	76.2	56.2	1.87	0.378	0.000580	0.000195	0.00031	0.00052
20.1	40.6	78.7	59.1	1.24	0.256	0.00264	0.000888	0.0021	0.0047
24.2	47.1	72.3	52.3	3.51	0.697	0.000570	0.000192	0.00016	0.00028
24.7	47.8	71.5	51.5	3.82	0.755	0.00120	0.000404	0.00031	0.00053
24.8	47.9	71.5	51.4	3.64	0.718	0.00265	0.000891	0.00073	0.0012
25.1	48.5	70.5	50.7	4.41	0.870	0.000571	0.000192	0.00013	0.00022
27.9	51.7	69.4	47.8	2.67	0.505	0.000648	0.000218	0.00024	0.00043
39.5	63.8	60.0	36.1	0.488	0.0806	0.000435	0.000146	0.00089	0.0018
49.3	72.3	50.6	27.7	0.111	0.0167	0.000367	0.000123	0.0033	0.0074
60.0	80.1	40.0	19.9	0.0373	0.00509	0.000213	0.0000716	0.0057	0.014
72.3	87.5	27.7	12.5	0.0181	0.00224	0.000174	0.0000585	0.0096	0.026
78.0	90.5	22.0	9.49	0.0147	0.00174	0.000160	0.0000538	0.011	0.031

TABLE A-12. Distribution of Uranium between NaCl-CaCl₂-XMgCl₂ Salt and Cu-15.8 at. % Mg-1.03 at. % U-Mg Alloy at 800°C

Metal						Salt			Distribution Coefficient	
Mg		Cu		U		U, wt %	UCl ₃ , mol %	MgCl ₂ , mol %	K _d , wt %/wt %	D, mol %/at. %
wt %	at. %	wt %	at. %	wt %	at. %					
6.71	16.3	88.8	82.6	3.43	0.85	0.000574	0.000204	2.65	0.00017	0.00024
6.28	15.4	89.2	83.5	3.52	0.88	0.0146	0.00524	7.15	0.0041	0.0060
6.29	15.4	89.1	83.4	3.64	0.91	0.0446	0.0161	10.7	0.012	0.018
6.28	15.4	89.2	83.5	3.66	0.92	0.177	0.0654	25.8	0.048	0.071
6.36	15.5	89.5	83.5	3.60	0.90	0.464	0.178	53.3	0.13	0.20
6.75	16.4	88.8	83.0	3.48	0.863	0.105	0.0387	24.3	0.030	0.045
6.37	15.6	88.9	83.2	4.16	1.04	0.322	0.122	46.4	0.077	0.12
6.18	15.2	89.0	83.6	4.22	1.06	0.367	0.140	46.4	0.087	0.13

TABLE A-13. Distribution of Uranium between NaCl-CaCl₂-XMgCl₂ Salt and Cu-16 at. % Mg Alloy at 800°C

Metal						Salt			Distribution Coefficient	
Mg		Cu		U		U, wt %	UCl ₃ , mol %	MgCl ₂ , mol %	K _d , wt %/wt %	D, mol %/at. %
wt %	at. %	wt %	at. %	wt %	at. %					
6.98	16.7	90.0	82.5	3.00	0.734	0.000784	0.000280	1.29	0.00026	0.00031
7.18	17.2	89.6	82.0	3.23	0.789	0.00339	0.00622	5.83	0.0011	0.0015
6.81	16.4	89.9	82.8	3.31	0.814	0.0217	0.00783	10.4	0.0066	0.0096
6.69	16.2	89.7	83.0	3.58	0.883	0.108	0.0397	24.7	0.030	0.045

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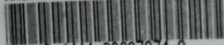
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REFERENCES

1. W. J. Walsh *et al.*, *Uranium Purification by the Salt-transport Process--Engineering Demonstration*, to be published as an ANL report.
2. H. M. Feder and I. G. Dillon, "Pyrometallurgical Processes," in *Reactor Handbook*, Vol. 2, *Fuel Reprocessing*, 2nd ed., p. 313, S. M. Stoller and R. B. Richards (eds.), Interscience Publishers, Inc., New York (1961).
3. E. Motta *et al.*, *Pyrometallurgical Processes: Process and Equipment Development*, TID-7534 (2), p. 719 (1957).
4. J. H. Schraidt and M. Levenson, "Developments in Pyrometallurgical Processing," in *Progress in Nuclear Energy, Series III, Process Chemistry*, Vol. 3, p. 329, F. R. Bruce, J. M. Fletcher, and H. H. Hyman (eds.), Pergamon Press, New York (1961).
5. F. S. Martin and G. L. Myles, "The Principles of High-temperature Fuel Processing," in *Progress in Nuclear Energy, Series III, Process Chemistry*, Vol. 1, p. 291, Pergamon Press, New York (1956).
6. L. Burris, Jr., *et al.*, *Recent Advances in Pyrometallurgical Processes*, *Trans. Amer. Nucl. Soc.* 4(2), 192 (1961).
7. S. Lawroski and L. Burris, Jr., *Processing of Reactor Fuel Materials by Pyrometallurgical Methods*, *At. Energy Rev.* 2(3), 3 (Oct 1964).
8. R. D. Pierce and L. Burris, Jr., *Pyroprocessing of Reactor Fuels, Reactor Technology, Selected Reviews*, L. E. Link, ed., TID-8540, p. 711 (1964).
9. L. Burris, Jr., *et al.*, "Pyrometallurgical and Pyrochemical Fuel Processing," in *Proceedings of 3rd International Conference on Peaceful Uses of Atomic Energy* 10, p. 501, International Atomic Energy Agency, Geneva (1965).
10. O. E. Dwyer, *Process for Fission Product Removal from Uranium-Bismuth Reactor Fuels by Use of Fused Salt Extraction*, *J. AIChE* 2, 163 (1956).
11. D. W. Bareis, R. H. Wiswall, and W. E. Winsche, *Processing of Liquid Bismuth Alloys by Fused Salts*, *Chem. Eng. Progr. Symp. Ser.* 50, 228 (1954).
12. O. W. Dwyer, R. J. Teitel, and R. H. Wiswall, "High Temperature Processing Systems for Liquid Metal Fuels and Breeder Blankets," in *Proceedings of International Conference on Peaceful Uses of Atomic Energy* 9, p. 604, IAEA, Geneva (1955).
13. R. H. Wiswall *et al.*, "Recent Advances in Chemistry of Liquid Metal Fuel Reactors," in *Proceedings of 2nd International Conference on Peaceful Uses of Atomic Energy* 17, 428 IAEA, Geneva (1958).
14. P. Chiotti, *Regeneration of Fission-product-containing Magnesium-Thorium Alloys*, U.S. Patent 3, 120, 435 (Feb 4, 1964).
15. P. Chiotti and J. S. Klepfer, *Transfer of Solutes between Liquid Alloys in Mutual Contact with Fused Salt. Application to Fuel Reprocessing*, *Ind. Eng. Chem. Process Design Develop.* 4(2), 232 (1965).

16. I. Johnson, "Partition of Metals between Liquid Metal Solutions and Fused Salts," in *Applications of Fundamental Thermodynamics to Metallurgical Processes*, G. R. Fitterer, ed., Gordon and Breach, New York (1967), pp. 153-177.
17. A. E. Martin, Argonne National Laboratory, personal communication (1968).

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